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The CO_2 Pulse Technique for Determining Residual Gas Life of Charcoal Beds

Part 1 - Bench-Scale Studies

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ABSTRACT

The CO_2 pulse method for determining the remaining adsorptive capacity, or residual gas life, of adsorbent charcoal beds has been carried out on a bench scale. This method depends on the dispersion, or broadening, of the CO_2 concentration pulse, or elution peak, when a dose of the gas is swept through the bed. A clean charcoal bed causes considerable dispersion of the elution peak; a fully spent bed has little effect. A partially spent bed broadens the elution peak to an extent which depends on the amount of adsorptive capacity remaining. This dispersion of the elution peak is essentially insensitive to relative humidity over the range from 10 to 70%. This method permits the nondestructive, in-place determination of residual gas life of a charcoal bed without interrupting its normal operation.

An adaptation of the CO_2 pulse method permits detection of leaks in a charcoal bed, such as those caused by channeling or faulty packing. A leak causes the CO_2 concentration pulse to emerge from the bed as a double peak–one lobe for the gas which penetrates the leak and the other for the gas which is eluted through the intact part of the bed.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

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THE CO_2 PULSE TECHNIQUE FOR DETERMINING RESIDUAL GAS LIFE OF CHARCOAL BEDS

Part 1 - Bench-Scale Studies

INTRODUCTION

Adsorbent charcoal is an effective agent for removing unwanted gases from an air stream. It is used in both large-capacity units for ventilating systems and small-capacity units for individual respirators. Charcoal cleans air by adsorbing and holding the contaminating gases. When its capacity is exhausted, the charcoal can no longer clean the air and must be replaced.

To assure adequate air-cleaning capacity without undue cost in material and labor, it is desirable to monitor the condition of the charcoal from time to time. The CO_2 pulse technique to be described provides an in-place, dynamic procedure which does not interrupt the normal operation of the adsorbent bed.

In using this method, one injects a dose of CO_2 into the air stream ahead of the adsorbent bed and observes the change in the timewise variation of the CO_2 concentration pulse, or elution peak, as the dose passes through the bed. The effect of the adsorbent bed on the shape of the elution peak is directly relatable to the residual adsorptive capacity of the bed.

This method has been described briefly with some examples of its application in a paper by Bogardus, Deitz, and Stamulis (1). The purpose of this report is to describe the method in more detail and to present the results of some developmental studies which provide a background for the method in its present form.

CO_2 is weakly adsorbed by carbon. Being weakly adsorbed, it can be readily eluted or swept away by a continuous air flow. An injected dose of CO_2 thus moves through a charcoal bed as a concentration-time pulse.

This pulse, or elution peak, becomes dispersed by three general effects: (a) diffusion within the gas stream, (b) viscous flow variations, and (c) holdup due to adsorption and desorption at the carbon surface. For a given charcoal bed and flow geometry, a and b are constant; c varies with the adsorptive capacity of the bed. A clean charcoal bed causes considerable dispersion (flattening and broadening) of the CO_2 pulse; a fully spent bed has very little effect on the shape of the pulse. A partially spent bed flattens and broadens the pulse to an extent which depends on the amount of adsorptive capacity remaining.

Figure 1 illustrates the change in the shape of a CO_2 elution peak emerging from a charcoal bed after successive increments of loading the charcoal with n-decane. For a given dose size and identical operating conditions, the integrated area of each elution peak (concentration-time product) is the same. The height increases and the width decreases as the adsorptive capacity is decreased by the addition of n-decane.

All other factors being accounted for, the shape of the elution peak of an adsorbate is determined by the shape of its adsorption isotherm. For a material whose adsorption

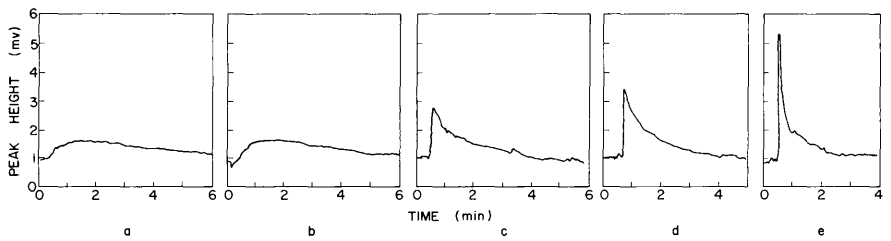


Fig. 1 - CO_2 elution peaks emerging from a charcoal bed loaded with successive increments of n-decane. The CO_2 dose volume was 0.1 cc; the flow rate through bed was 1 l/min; the amplifier gain setting was 900; the coupling potentiometer setting was 810. (a) 0 g decane/g charcoal (b) 0.03 g decane/g charcoal (c) 0.08 g decane/g charcoal (d) 0.12 g decane/g charcoal (e) 0.18 g decane/g charcoal.

isotherm is concave to the pressure axis (Langmuir, or Type I, isotherm) (2), the elution peak is skewed with a sharp front and a long tail (3). The degree of asymmetry and the length of the tail are related to the affinity and capacity for adsorption.

The Type I isotherm can be described by an expression of the form

$$V = \frac{k_1 k_2 p}{(1 + k_1 p)},$$

where V is the amount of gas adsorbed, p is the pressure, and k_1 and k_2 are constants (3). The affinity constant k_1 is related to the energy of adsorption at the sites concerned. Increasing k_1 increases the curvature of the isotherm toward the pressure axis and hence the amount of tailing of the related elution peak. The capacity constant k_2 is related to the total number of available sites. Increasing k_2 increases the amount of adsorption and hence also increases the amount of tailing of the related elution peak. CO_2 adsorbed on charcoal follows a Type I isotherm. Thus, a CO_2 elution peak emerging from a clean charcoal bed appears as curve a in Fig. 1. As the charcoal bed is progressively loaded with decane, both the number of available sites and the average energy of adsorption at these sites is decreased. Hence, the shape of the CO_2 elution peak changes progressively toward the form of curve e in Fig. 1.

EXPERIMENTAL METHOD AND APPARATUS

The apparatus for conducting a CO_2 pulse experiment is arranged as shown schematically in Fig. 2. The various components and their functions are described in the following paragraphs.

Air Source

For some of the CO_2 pulse experiments, laboratory compressed air at controlled values of relative humidity was used as the carrier gas. The compressed air was passed through an Ascarite column to remove any background CO_2 and then through either a drying column or a humidifying apparatus to achieve the desired relative humidity. The humidifier used was the pressurized saturator which was described by Lawrence and Bogardus (4). This device was capable of providing air at relative humidities from 40 to 95%, accurately controlled to ± 1%.

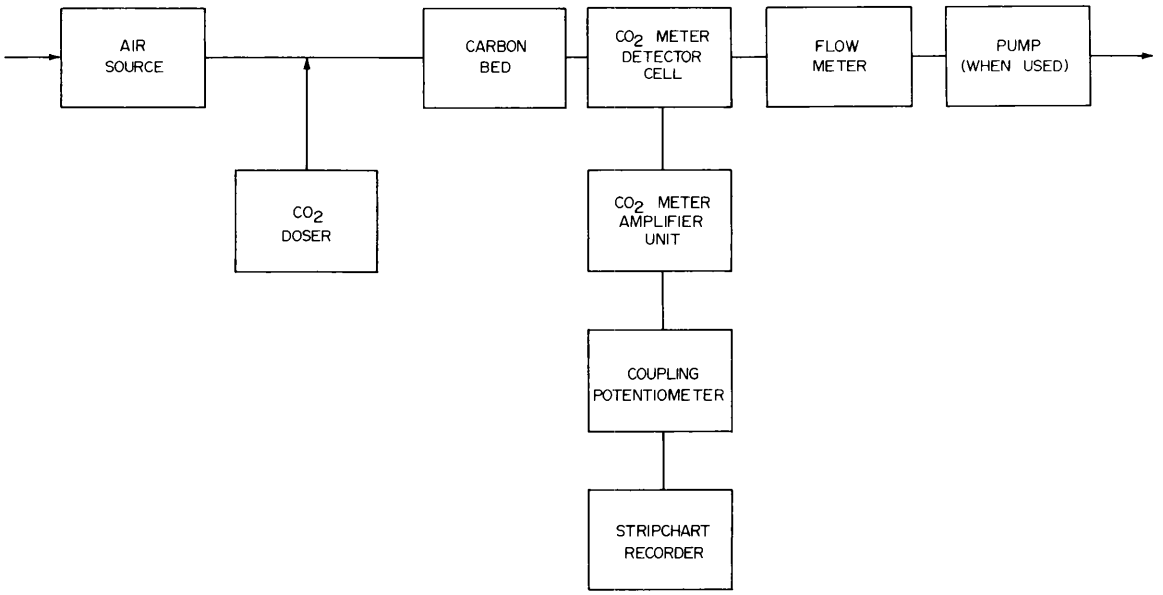


Fig. 2 - Apparatus for evaluating the residual life of charcoal beds by the CO_2 pulse method

For other studies, ambient room air was used as the carrier gas rather than compressed air. In these experiments the room air was drawn through the system by means of a rotary carbon vane pump at the downstream end of the system.

Flow Meter

Airflow rates were measured by a floating ball flow meter located downstream from the CO_2 detection cell. For some experiments (on beds of large cross-sectional area) the airflow rate through the carbon bed was high enough that the stream had to be divided to send only a portion through the detection cell.

CO_2 Doser

Small doses of CO_2 were injected quickly into the air stream by means of hypodermic syringes of suitable capacity. Large doses (over 1 cc) were admitted through a quick-release valve from a pressurized container of known volume.

Carbon Bed and Container

The charcoal beds were contained in glass tubes, or cells, typically about 2 cm^2 in cross-sectional area. These cells were fitted with O-ring glass joints at each end for attachment to the apparatus. Metal screens and disks of filter paper served to hold the packed carbon granules in place in the cells. The charcoal was packed into the cells by means of a sifter filler* to assure random fall and close packing of the charcoal granules.

*The sifter is a device designed for filling respirator canisters. By dropping through a series of strategically placed screens, charcoal granules fall in a random pattern and form a uniform, closely packed bed in the canister.

CO_2 Meter

The CO_2 concentration in the gas stream was measured by means of a Beckman Medical Gas Analyzer, Model LB-1 (Ref. 5). This is an ID absorption instrument which, with proper filters, responds specifically to CO_2. The instrument has two major components, the detecting cell and the indicator-amplifier unit. In the detecting cell, the IR absorption of the unknown gas is compared with that of a CO_2-free reference gas. Any difference in IR absorption due to CO_2 in the unknown gas causes unequal heating and induces a change of electrical capacitance in the cell. This capacitance change is then translated by the indicator-amplifier unit and displayed as percent CO_2.

The output of the indicator-amplifier unit is coupled to a fast-response strip chart recorder by means of a 25-ohm multiturn potentiometer connected as a voltage divider. Both this potentiometer and the gain control potentiometer on the amplifier were fitted with locking vernier dials to facilitate making reproducible settings.

The recorder used was a Varian Model G-11A instrument (6). This recorder has nine spans from 10 mv to 100 v; its full-span balancing time is 1 sec.

The nominal range of the Beckman gas analyzer is 0 to 10% CO_2. For most of the studies reported here, the instrument was operated near its maximum sensitivity, i.e., near maximum gain in the amplifier. Calibration of the overall system response was obtained by sampling standard mixtures of CO_2 and air or nitrogen. Response was not linear; so the system had to be calibrated at several intervals over the total range.

In experiments where the total airflow rate was low (approximately 1 l/min), the whole air stream was passed through the IR cell. When the total airflow rate was larger, the air stream was divided and only a part was sampled by the IR meter. Under these latter conditions, especially, the measured concentration of CO_2 was rather low, and a high gain was required on the amplifier.

Agent Loading Method

For some of the experiments the charcoal beds had to be loaded with known quantities of chemical agents, such as n-decane or methyl acetoacetate. This was done by passing an air stream through a temperature-controlled bubbler filled with the appropriate liquid agent and then through the charcoal bed. Concentrations of about 3 mg decane/l were obtained in this way, for example. The amount of agent adsorbed by the charcoal was determined by weighing the sample cell and contents.

During the loading process, it was necessary to detect the breakthrough point of the charcoal bed (i.e., the point at which agent vapor started to come through the bed). For this purpose the effluent air stream was passed first through a combustion furnace containing Hopcalite and then into the IR detecting cell. Hopcalite is a proprietary mixture of metal oxides, which, when heated to about 400° C, catalyzes the conversion of hydrocarbons and related organic compounds into CO_2 and H_2O. (These are the principal products. There may also be traces of CO, which are not significant here.) Thus, when the breakthrough occurred, the Beckman instrument detected the effluent agent concentration as its equivalent in CO_2. For decane, this breakthrough concentration was arbitrarily chosen to be about 0.08 mg/l. This concentration of decane corresponded to 0.01 vol-% CO_2 or about a 1-mv deflection on the CO_2 meter. Figure 3 shows the schematic arrangement of apparatus for loading the charcoal beds and detecting the breakthrough concentrations of the agent vapor.

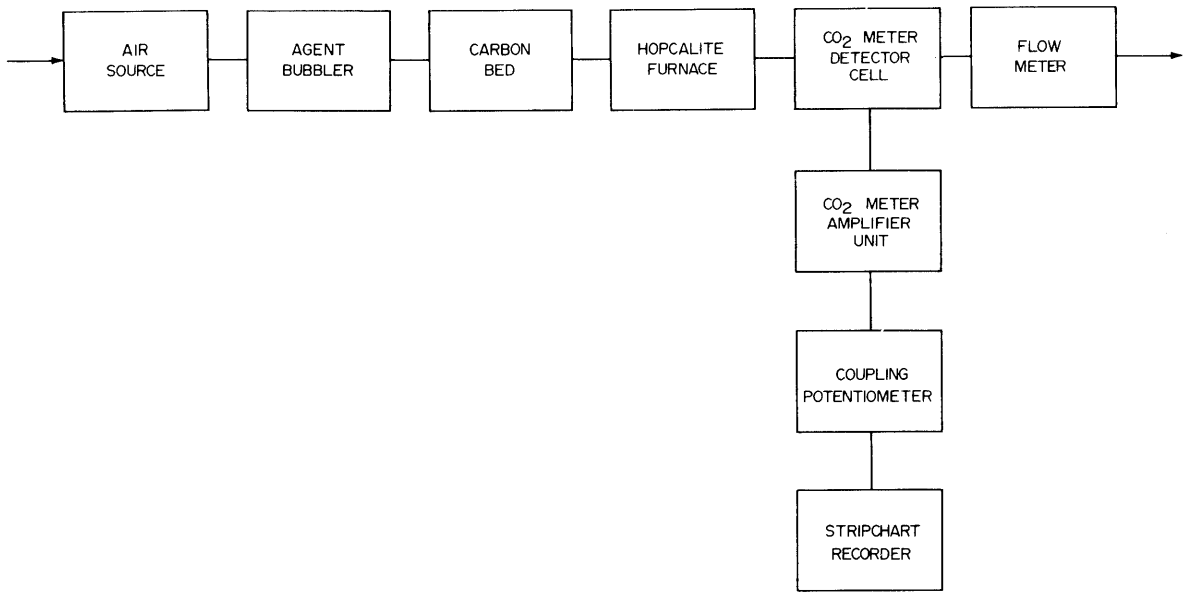


Fig. 3 - Apparatus for loading the charcoal beds with the agent vapor

Conduction of a CO_2 Pulse Experiment

The method of conducting a CO_2 pulse experiment is as follows:

After the apparatus is prepared and the carbon bed put in place, the air stream is started at the desired flow rate. The CO_2 meter and recorder are adjusted to compensate for background CO_2 and to establish a base line (5,6). Then a dose of CO_2 is injected, and the resulting concentration pulse, or elution peak, is recorded. The height and/or width of the peak is noted. The process is repeated for other charcoal beds which are to be compared. The adsorptive capacity or residual life of an unknown charcoal bed is estimated from a comparison of its CO_2 elution peak with those for a clean bed and for a standard contaminated bed which is otherwise identical to the unknown bed. (A standard contaminated bed is one which has been loaded to its break point with a chemical agent to simulate a completely spent bed.)

It is apparent from the foregoing descriptions that there are many variables, both experimental and instrumental, which may affect the shape of a CO_2 elution peak as it finally appears on a recorder chart. Instrumental factors include several electrical and mechanical adjustments, such as amplifier gain, coupling potentiometer ratio, recorder span, chart speed, optical alignment of the IR cell, and mechanical and electrical balance of the zero point.

Experimental factors include various conditions, such as temperature, airflow rate, IR cell sampling rate, relative humidity, charcoal bed depth, and CO_2 dose size. All these factors must be either constant or compensated for if the performance of different charcoal beds is to be compared.

The studies to be described in this report led to choosing and specifying the optimum experimental conditions, instrument settings, and calculation procedures for applying the CO_2 pulse method to the determination of residual adsorptive capacity or residual life of a charcoal bed.

RESULTS

Calibration of Response of the System

Several factors affect the response of the CO_2 meter: mechanical and electrical zero adjustment of the indicator-amplifier unit, amplifier gain, and optical balance or alignment of the IR cell. Since variations in any of these quantities will affect the overall response, it is necessary to fix them as prescribed by the instruction manual for the CO_2 meter (5) and then to calibrate the system in terms of standard mixtures of gas.

The data in Table 1 and Figs. 4 and 5 show the response of the CO_2 meter to some typical mixtures of gas. The estimate of 0.03% CO_2 for room air is the value given in the Handbook of Chemistry and Physics (7) as the average CO_2 content of the atmosphere. It is to be seen in Fig. 4 that the response of the meter is approximately linear with CO_2 concentration over short ranges. It is also to be seen in Fig. 5 that, for a given CO_2 concentration, the meter response is approximately proportional to the logarithm of the amplifier gain setting.

Table 1
Response of the CO_2 Meter as a Function of Gas Concentration and Amplifier Gain

Amplifier Gain, Dial Setting*	Log_{10} Amplifier Gain/100	Coupling Potentiometer, Dial Setting*	Gas in Cell	Recorder Deflection (mv)
500	0.699	810	CO_2-free air	0
			Room Air (approx. 0.03% CO_2)	1.9
			0.65% CO_2 in N_2	26.5
750	0.875	810	CO_2-free air	0.7
			Room Air	1.6
			0.65% CO_2 in N_2	32.0
900	0.954	810	CO_2-free air	0.7
			Room air	1.6
			0.65% CO_2 in N_2	34.0
900	0.954	810	CO_2-free air	0
			Room air	1.5
			0.64% CO_2 in N_2	39.0
			1.58% CO_2 in air	81.0
			2.65% CO_2 in air	124.0
			3.46% CO_2 in air	146.0

*Full scale on dial is 1000

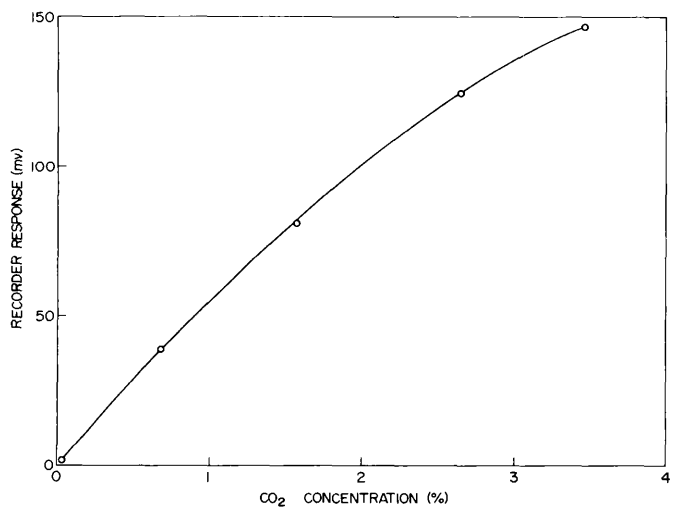


Fig. 4 - Response of the CO_2 meter as a function of CO_2 concentration. The meter amplifier gain setting was 900; the coupling potentiometer setting was 810.

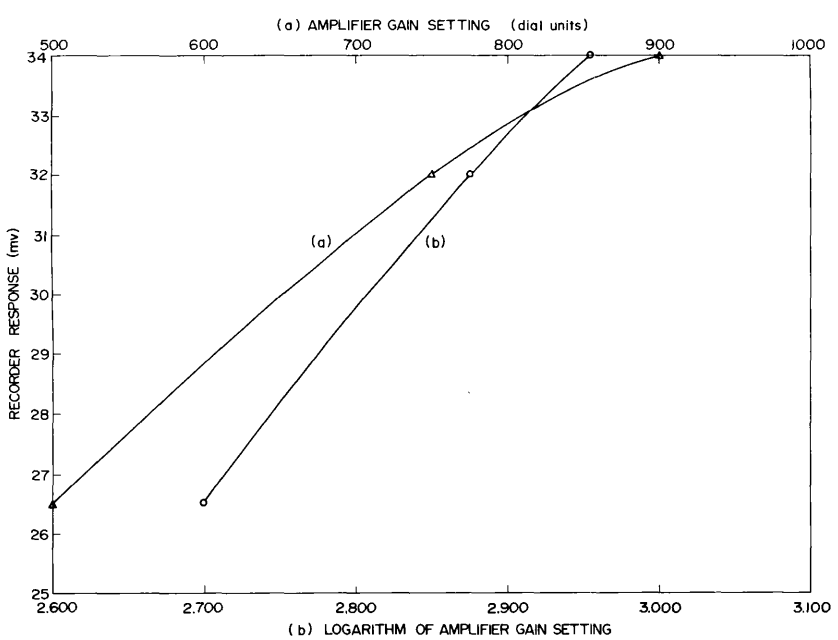


Fig. 5 - Response of the CO_2 meter as a function of (a) amplifier gain setting and (b) $\log_{10}$ of amplifier gain setting. The CO_2 concentration was 0.65%.

Effect of Varying Instrument Settings at Constant Dose and Flow Rate

Table 2 and Fig. 6 show the effect on net difference in peak height as the amplifier gain and the coupling potentiometer settings are increased independently. For each of a series of fixed settings on the one dial, the other was varied over its entire range. The product of the two dial settings was recorded for each meter reading (i. e., 700 on the amplifier gain dial and 400 on the coupling potentiometer dial were recorded as 28×10^4). Each entry in Table 2 and each point in Fig. 6 represent an average of a number of readings and has a precision of about ±3%. Results are given both for a charcoal bed and for an empty cell. There is a linear relationship in each case, which appears to contradict the data presented earlier in the discussion on calibration, where a logarithmic variation was found between the amplifier gain and the instrument response. However, it should be noted that the earlier data (Fig. 5) covered a meter response range of 34 mv, nearly seven times that reported in Fig. 6. The system is more nearly linear in response over this limited range.

Table 2
Effect of Varying the Instrument Settings at Constant Dose Size* and Flow Rate*

Product of Amplifier Gain Setting times Coupling Potentiometer	CO_2 Elution Peak Height With the Coupling Potentiometer Fixed and the Amplifier Gain Varied (mv)	CO_2 Elution Peak Height With the Amplifier Gain Fixed and the Coupling Potentiometer Varied (mv)
Charcoal Bed		
10×10^4	0.2	0.2
20×10^4	0.4	0.4
30×10^4	0.65	0.6
40×10^4	0.85	0.75
50×10^4	1.0	1.0
60×10^4	-	1.2
70×10^4	1.4	1.2
80×10^4	1.55	1.55
Empty Cell		
10×10^4	0.65	0.65
20×10^4	1.35	1.2
30×10^4	2.05	1.9
40×10^4	2.65	2.6
50×10^4	3.2	3.2
60×10^4	3.85	3.8
70×10^4	4.35	4.3
80×10^4	4.7	5.1

*The flow rate was 3.7 l/min through the bed and 1.0 l/min through the IR cell; the CO_2 dose volume was 3cc.

Although the nominal range of the Beckman meter is 0 to 10%, its linearity is limited to short ranges of gas concentration and gain setting. Hence, it is desirable to plan an experiment so that measurements can be confined to these limited ranges.

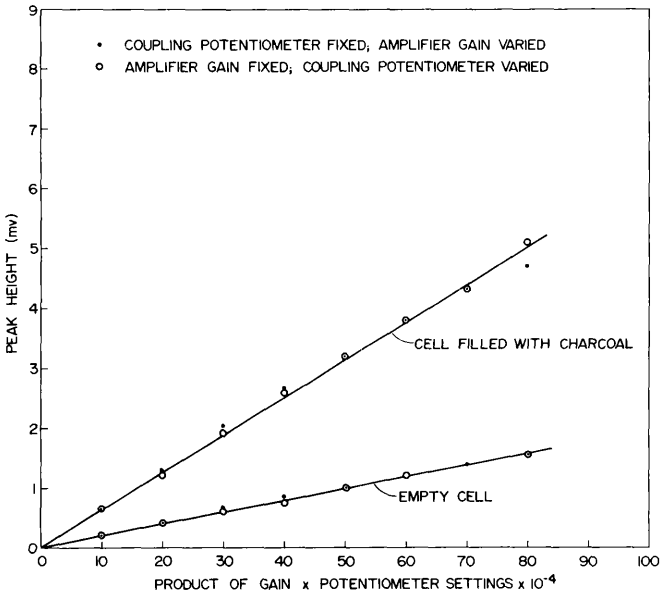


Fig. 6 - CO_2 elution peak height as a function of the product of amplifier gain and the coupling potentiometer dial settings. The CO_2 dose volume was 3 cc.

Effect of CO_2 Dose Size in Relation to Flow Rate

The shape of the CO_2 elution peak depends to some extent on the flow rate through the bed in relation to dose size. As shown by the peaks in Fig. 7, a given dose passing at a slow rate tends to reach a constant concentration for a short time. This results in an apparent flattening of the elution peak at its maximum. As the flow rate is increased, there is less time to reach a steady state, and the peak becomes more sharply curved. The implication here is that one should choose a dose size in relation to flow rate so that a steady concentration will not be reached at any time. The dose should be large enough to be easily detectable but not large enough to broaden the elution peak.

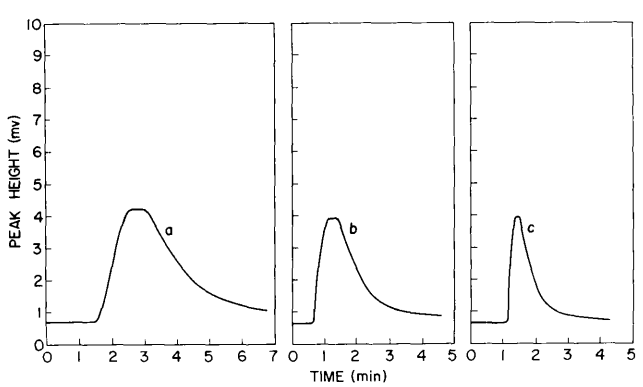


Fig. 7 - Effect of the flow rate on the shape of CO_2 elution peak. The CO_2 dose volume was 1 cc. The flow rate through bed was (a) 1/2 l/min, (b) 1 l/min, and (c) 1.7 l/min.

Effect of CO_2 Dose Size at Constant Flow Rate

Table 3 and Fig. 8 show the effect of increasing dose size at a constant flow rate through the bed and the cell. In all cases the dose sizes were small enough that a steady concentration was never reached. It is to be seen that the net difference in peak height between the charcoal bed and the empty cell increases approximately with dose size.

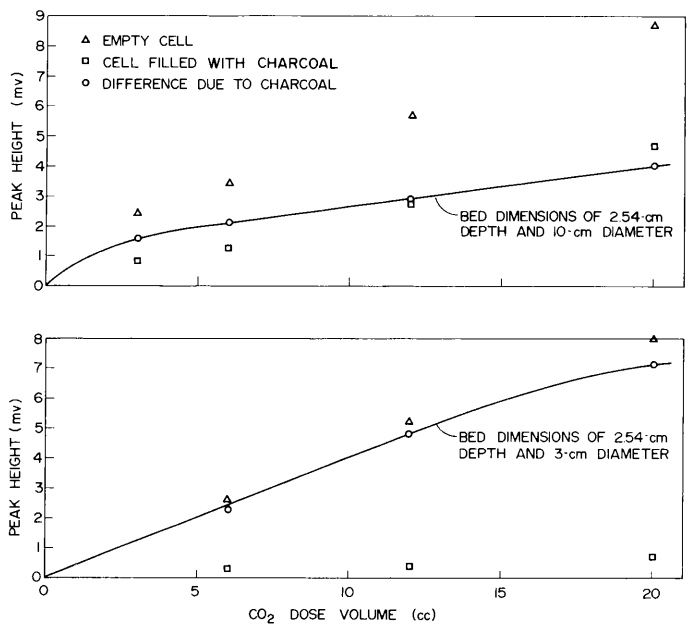


Fig. 8 - CO_2 elution peak height as a function of dose volume

Effect of Increasing Flow Rate Through the Bed at a Constant Rate of Sampling

Table 4 and Fig. 9 show the effect of increasing the flow rate through the charcoal bed, while maintaining a constant sampling rate through the IR detector cell. There is an inverse relationship between elution peak height and the flow rate through the charcoal bed. As the bed flow rate increases, the concentration in the sampling stream must decrease.

Effect of Bed Depth on CO_2 Peak Height and Width

All other things being equal, it might be expected that the capacity of a charcoal bed could be increased by increasing the bed depth. The effect of the bed depth on the shape of the CO_2 elution peak was investigated for two representative samples of protective mask charcoal.

Both samples were nominal 12-30 mesh, PCC-ASC* impregnated charcoals. Sample A was taken from a laboratory stock barrel; this charcoal had been manufactured about 1958. Sample B was taken from a protective mask canister which had been manufactured in 1948.

*PCC-ASC impregnated charcoal is the adsorbent currently used in navy canisters. It is a coke-based charcoal which has been impregnated with a number of heavy metal catalysts for use against various toxic gases.

Table 3
Effect of Dose Size on Peak Height

Dose Volume of CO_2 (cc)	Peak Height for Charcoal Bed (mv)	Peak Height for Empty Cell (mv)	Peak Height Difference Height (Cell) - Height (Charcoal) (mv)	Amplifier Gain Setting*	Coupling Potentiometer Setting*
Bed with a 3-cm diameter and a 2.54-cm depth					
6	0.3	2.6	2.3	700	135
12	0.4	5.2	4.8	700	135
20	0.7	8.0	7.1	700	135
Bed with a 10-cm diameter and a 2.54-cm depth					
3	0.85	2.4	1.6	150	250
6	1.30	3.4	2.1	150	250
12	2.75	5.7	2.9	150	250
20	4.70	8.7	4.0	150	250

*Full scale on dial is 1000.

Table 4
Effect of Flow Rate Through Bed on Peak Height*

Peak Height For Charcoal Bed (mv)	Peak Height For Empty Cell (mv)	Peak Height Difference, Height (Cell) - Height (Charcoal) (mv)	Flow Rate Through Bed (l/min)
0.7	6.0	5.3	24
0.7	3.0	2.3	41
0.5	2.0	1.5	66

*The CO_2 dose volume was 5.3 cc; the flow rate through the IR cell was 0.5 l/min; the charcoal bed depth was 2.54 cm.

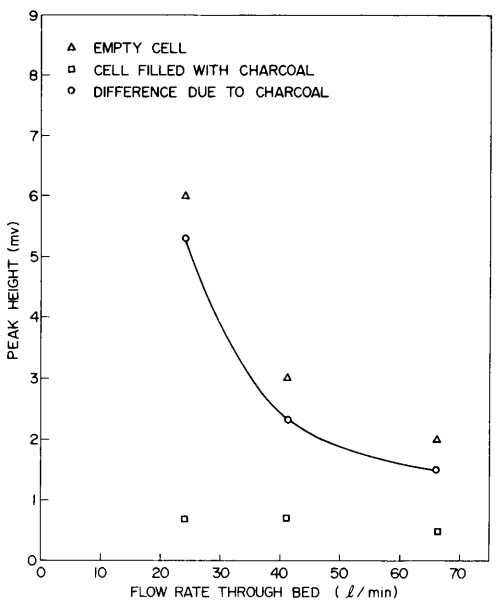


Fig. 9 - CO_2 elution peak height as a function of flow rate through the bed

The data in Table 5 show the CO_2 peak height vs the corresponding bed depths. Plotting peak height vs bed depth gives a continuous curve (Figs. 10a and 10b). There is no obvious simple theoretical relationship between elution peak height and bed depth. That is, the curves in Figs. 10a and 10b cannot be made linear by the usual techniques of plotting powers or reciprocals of one variable.

Effect of Leaks in a Charcoal Bed

When a CO_2 pulse is passed through a charcoal bed and the elution peak observed, the premise is that the charcoal bed is intact. In any practical case, an occasional leak may be found for one reason or another. Leaks might be caused by loose or irregular packing of the carbon granules, by foreign bodies accidentally getting mixed with the charcoal, or by faulty hardware or assembly. The elution peaks in Fig. 11 show the effect of an intentionally placed leak in a charcoal bed. The leak was a capillary tube placed so that it went through the otherwise intact bed packing. The cross-sectional area of the charcoal bed was 202 mm^2; the cross-sectional area of the leak was 0.788 mm^2. Airflow rates varied from 1/4 l/min to 2 l/min. It is to be seen that at the lower flow rates a well-defined double peak appeared. The first lobe was due to the CO_2 coming through the leak; the second lobe was due to the CO_2 which took the slower route through the adsorbent bed.

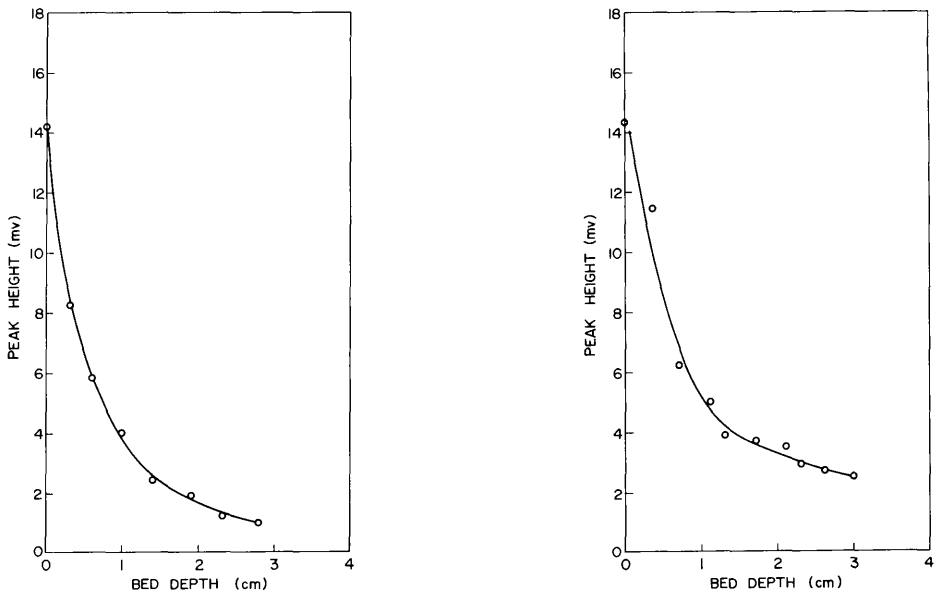
Table 5
Effect of Charcoal Bed Depth on
Elution Peak Height

Weight of Charcoal (g)	Bed Depth (cm)	Peak Height (mv)
Sample A, Barrel, 1968		
2.3120	2.8	1.0
1.8744	2.3	1.2
1.4715	1.9	1.9
1.1362	1.4	2.4
0.7905	1.0	4.0
0.5006	0.6	5.8
0.2440	0.3	8.2
Empty Cell	0.0	14.2
Sample B, Canister, 1948		
3.1777	3.0	2.5
2.6527	2.6	2.7
2.4022	2.3	2.9
2.0466	2.1	3.5
1.7354	1.7	3.7
1.3862	1.3	3.9
1.1287	1.1	5.0
0.7357	0.7	6.2
0.3362	0.35	11.4
Empty Cell	0.0	14.3

Effect of Humidity on the CO_2 Elution Peak

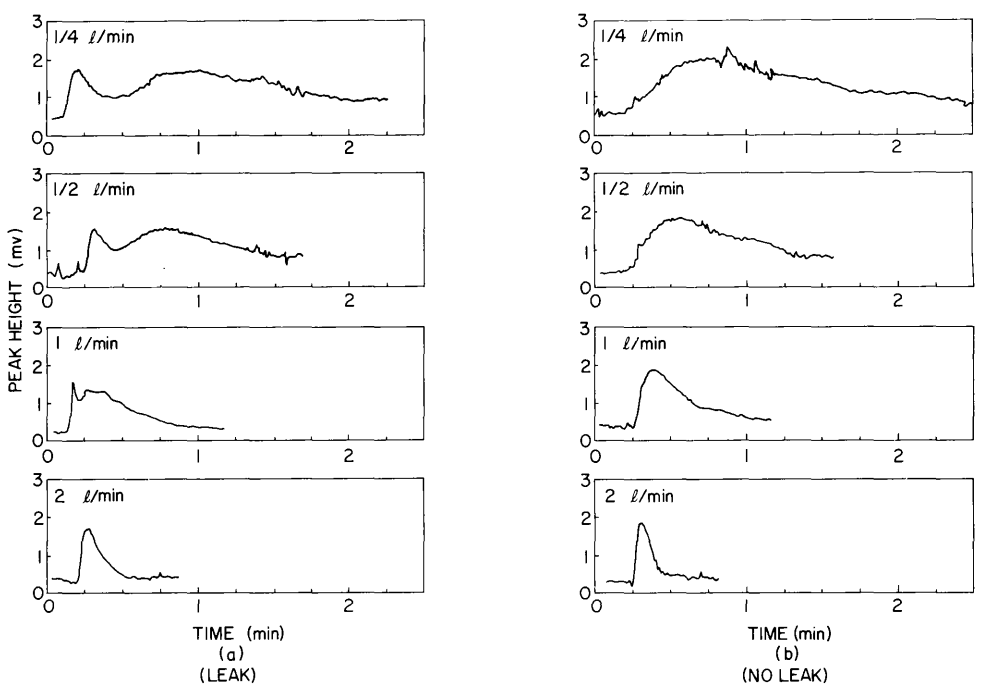
CO_2 and H_2O are both involved in the so-called "surface complex" that exists on charcoal surfaces (8). So, it might be expected that moisture would affect the shape of a CO_2 elution peak.

The data in Table 6 show the results of a series of observations on the effect of various charcoal conditioning treatments on the CO_2 peak shape. In each series, the effect of purging with dry air or N_2 and of purging at elevated temperatures is to increase the CO_2 peak height. The charcoal as received undoubtedly had some moisture content; purging by dry gas or heated gas would remove this moisture. Since the result of purging was to increase the peak height and thus to decrease the "tailing," it might be inferred that water adsorbed on the charcoal had enhanced the adsorptive capacity for CO_2.



(a) Barrel charcoal (b) Canister charcoal

Fig. 10 - CO_2 elution peak height as a function of the charcoal bed depth



(a) (b)

Fig. 11 - CO_2 elution peaks for a charcoal bed containing (a) an intentionally placed leak and (b) no leak. The CO_2 dose volume was 0.1 cc.

Table 6
Effect of Various Preconditioning Treatments on the Elution Peak Height

Preconditioning Treatment (Done Consecutively in Order Shown)	Weight of Charcoal Bed (g)	Peak Height (mv)
Sample 1		
Original condition	1.7230	1.2
1-hour dry-air purge, room temperature	1.6516	2.5
1-hour dry-air purge, 160° C	1.5989	2.6
17-hour dry-air purge, 160° C	1.5771	2.8
1-hour dry-air purge, 196° C	1.5694	2.8
1-hour dry-air purge, 296° C	1.3292	3.4
Sample 2		
Original condition	1.7112	0.5
1-hour dry-air purge, room temperature	1.6158	0.8
2-hour dry-air purge, room temperature	1.6142	0.8
2-hour dry-N_2 purge, room temperature	1.6120	0.8
1-hour dry-air purge, room temperature	1.6130	1.0
1-hour dry-air purge, 150° C	1.5733	2.0
Sample 3		
Original condition	1.7034	0.4
1-hour dry-air purge, room temperature	1.6116	0.6
2-hour dry-air purge, room temperature	1.6065	1.6
1-hour dry-air, 1-hour dry-N_2 purge, room temperature	1.6086	0.4
2-hour dry-N_2, 1-hour dry-air purge, room temperature	1.6049	1.4
1-hour dry-air purge, room temperature	1.6049	1.4
16-hour dry-air purge, room temperature	1.5656	2.5
1-hour heating, 1-hour dry-air purge, 150° C	1.5649	2.5

When a charcoal bed is exposed to an air stream for an appreciable time, it becomes equilibrated to the relative humidity of the air. Figure 12 shows the results of a study of the effect of this equilibration on the CO_2 elution peak. The experiment started with dry charcoal. It was then equilibrated to an air stream whose relative humidity was increased stepwise to near saturation. Equilibration of the charcoal to each increment in relative humidity was assumed when the sample ceased to gain in weight.

CO_2 elution peaks were recorded at each stage of humidification. The peak heights were plotted vs relative humidity in Fig. 12. Then the relative humidity of the air stream was decreased stepwise, and CO_2 peaks were again recorded after equilibration at each step. The whole process was repeated two times. Figure 12 shows that there was a considerable difference between CO_2 peak heights on the adsorption and desorption branches of the first cycle, but this difference tended to decrease with successive cycles. This coming together of the adsorption and desorption branches may be similar to the "conditioning effect" often seen when determining gas adsorption isotherms repeatedly on a charcoal sample (9).

A point worthy of note in this study is the apparent plateau in peak heights between approximately 10 and 70% R.H. after the charcoal had been conditioned by cycling.

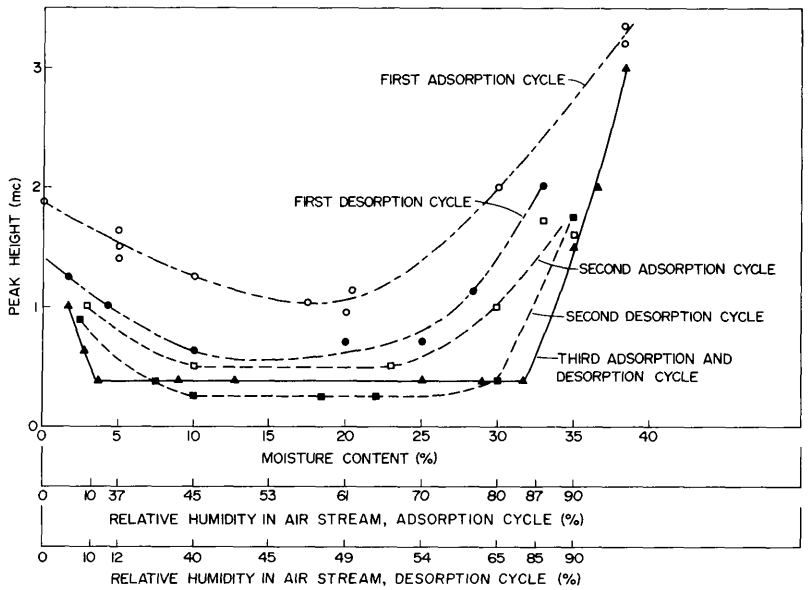


Fig. 12 - CO_2 elution peak height as a function of moisture content of charcoal. Relative humidity scales on adsorption and desorption are shown corresponding to the moisture content of the charcoal.

Effect of Loading Adsorbent Bed with Organic Vapors

The dispersion of a CO_2 elution peak is caused by holdup due to adsorption and desorption of CO_2 at the carbon surface. As this surface becomes progressively blocked by previously adsorbed materials, the dispersion of the CO_2 peak is expected to be decreased. In the following series of studies, charcoal beds were loaded stepwise with increasing quantities of organic vapors, and the effect on the CO_2 elution peak was observed at each step. For each increment of organic loading, the charcoal bed was cycled and equilibrated stepwise over the whole relative humidity range from 0 to 95%. CO_2 elution peak height was thus recorded as a function both of agent loading and of relative humidity.

The complete series was run first with n-decane as the adsorbed agent and then with methyl acetoacetate (MAA). N-decane was chosen as a typical heavy hydrocarbon which was available in a fairly pure state; MAA was chosen because it is a commonly used nontoxic simulant for GB (nerve gas).

The results for n-decane are summarized and presented in Fig. 13; MAA results are presented in Fig. 14. The figures show the CO_2 elution peak height as a function of relative humidity for each increment of organic vapor loading. As was mentioned early in this report, Fig. 1 shows a series of elution peaks at a single relative humidity (50%) for a charcoal bed loaded with successive increments of n-decane.

Figure 15 shows the variation of elution peak height with loading of n-decane for three values of relative humidity–10, 50, and 70%. Figure 16 shows comparable data for MAA. As Figs. 13 and 14 show, there is a plateau in elution peak heights over a middle range of relative humidity from about 10 to 70%. Within this range of relative humidity the variation of peak height with loading is about the same as that typified by the 50% R. H. data.

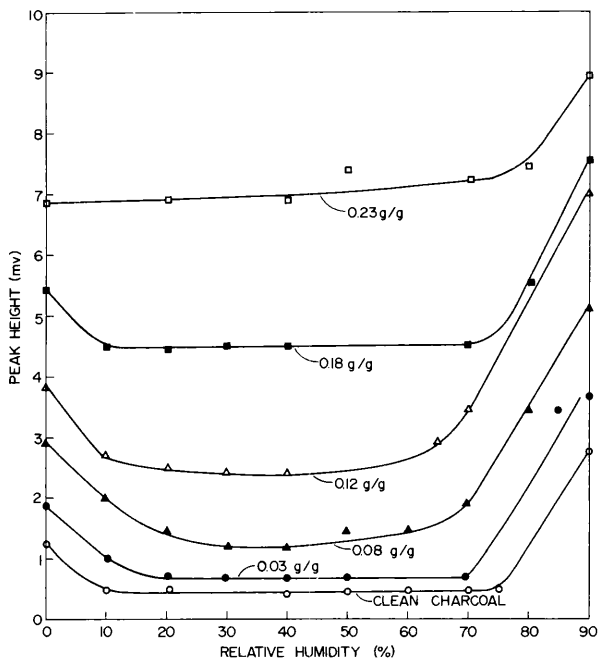


Fig. 13 - CO_2 elution peak height as a function of the relative humidity at various increments of n-decane loading. The CO_2 dose volume was 0.1 cc; the flow rate was 1 l/min; the break-point loading was 0.18 g/g.

Calculation of Residual Life

By definition, the loading at which a specified concentration of agent appears in the effluent air stream is called the "break point." (For a toxic agent, this specified concentration is related to the minimum toxic concentration.) At this loading the charcoal is said to have zero residual life. By definition, a charcoal with no agent adsorbed on it has 100% residual life. The residual life of a partially loaded charcoal is obtained from the difference between the break-point loading and the actual loading divided by the break-point loading; multiplying this fraction by 100 gives the residual life in percent. If x is the weight of agent adsorbed per gram of partially loaded charcoal and 0.18 is the weight adsorbed at the break point (for the decane and MAA studies reported here), the residual life of the partially loaded sample is given by

$$\frac{0.18 - x}{0.18} \times 100 = \text{residual life } (\%).$$

Residual lives calculated from the weight of agent adsorbed by charcoal samples loaded with n-decane are presented in Table 7. Those calculated for samples loaded with MAA are presented in Table 8.

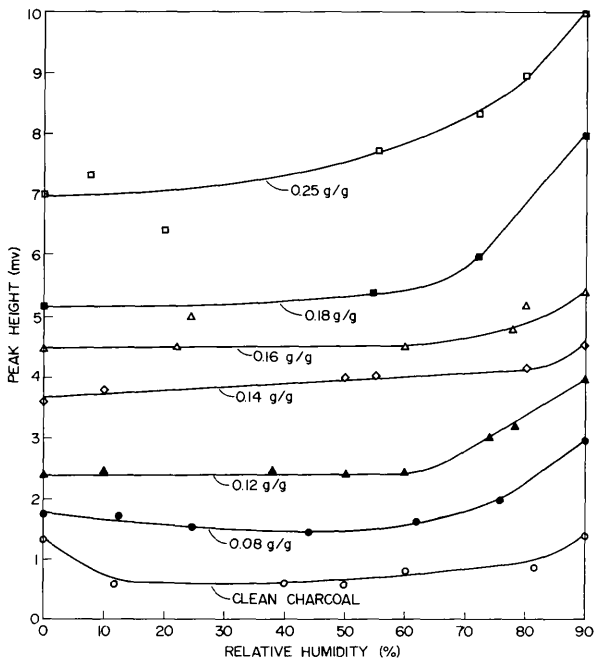


Fig. 14 - CO_2 elution peak height as a function of the relative humidity at various increments of MAA loading. The CO_2 dose volume was 0.1 cc; the flow rate was 1 l/min; the amplifier gain setting was 900; the coupling potentiometer setting was 810; the break-point loading was 0.18 g/g.

The residual life of a charcoal in terms of CO_2 elution peak heights is determined from three peak height measurements: one for a clean charcoal, one for a standard charcoal loaded to the break point, and one for the unknown partially loaded charcoal. These quantities are defined as elution peak height for the clean charcoal (C), elution peak height for the charcoal loaded to the break point (L), and elution peak height for the unknown charcoal (U). The fraction (L - U)/(L - C) is a function of the residual life of the charcoal. That is,

$$\left[\frac{(L - U)}{(L - C)}\right]^n = \left[\frac{(0.18 - x)}{0.18}\right]$$

and

$$\left[\frac{(L - U)}{(L - C)}\right]^n \times 100 = \text{residual life } (\%),$$

where the exponent n is an empirical quantity used to fit the peak height variable to the gravimetric data. It should be apparent from Figs. 13 through 16 that n may not always be the same. However if n equals 2, the above expression will fit the bulk of the available data in the relative humidity range from 10 to 70%. These results are presented in Table 7 (n-decane) and Table 8 (MAA).

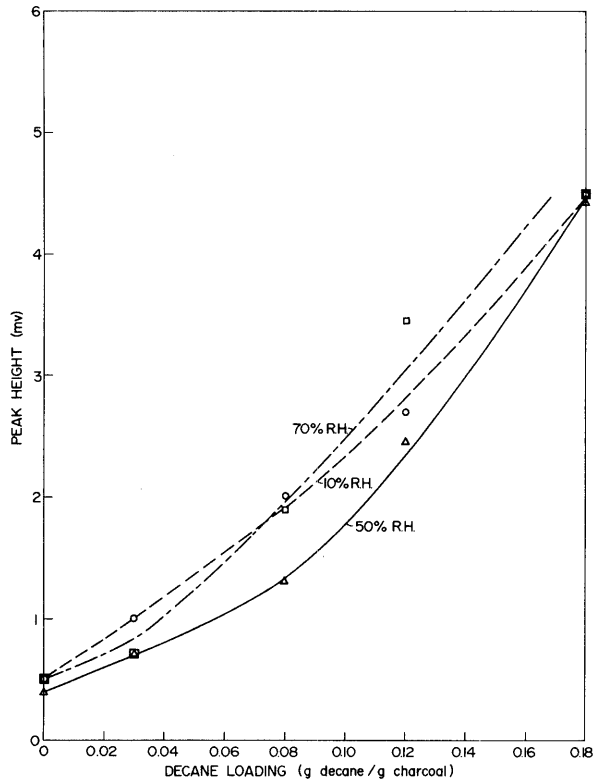


Fig. 15 - CO_2 elution peak height as a function of n-decane loading at three values of relative humidity

SUMMARY

The CO_2 pulse technique for evaluating the residual life of charcoal adsorbent beds is described. Details of the method and apparatus are described, along with the results of some background studies with appropriate comments.

The results point to some generalizations about the best conditions for conducting an experiment of this sort:

1. Because of the limited range of linearity of response of the CO_2 meter, experiments should be designed so that the CO_2 concentration stays within a range of about 0.1% above background. A range of 0.1% CO_2 concentration corresponds to a range of a few millivolts meter response.

2. The CO_2 dose volume should be kept small, commensurate with detectability to prevent momentary steady-state concentrations which cause flat-topped elution peaks.

3. When different elution peaks are to be compared, all factors affecting flow geometry must be as near alike as possible.

4. Because of the effect of humidity on the shape of the elution peak, all comparisons should be made under comparable conditions of relative humidity.

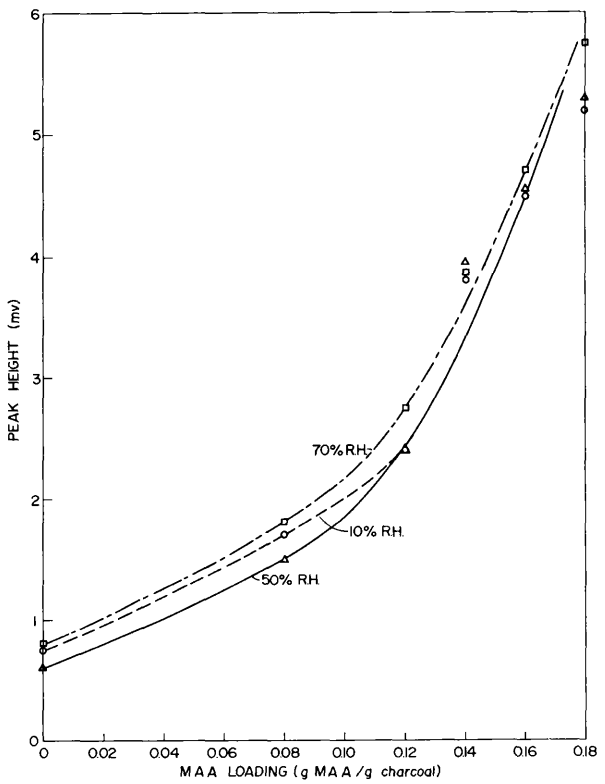


Fig. 16 - CO_2 elution peak height as a function of MAA loading at three values of relative humidity

Data are presented to show that the method can give a reliable measure of charcoal loading in terms of heavy organic vapors over a relative humidity range from 10 to 70%. Fortunately, this is the relative humidity range in which most practical measurements will be made. With special attention to the effect of humidity on the elution peak height-vapor loading relationship, the method can probably be used over wider ranges of relative humidity.

The CO_2 pulse technique is shown also to be capable of detecting simulated leaks in a charcoal bed when flow conditions were such as to permit the CO_2 to travel through the leak channel faster than through the intact part of the bed.

Table 7
Residual Life Calculated from n-Decane Adsorption and from CO_2 Elution Peak Height at Three Relative Humidities

Weight of Decane per Gram of Charcoal (g/g)	Residual Life from Decane Adsorption (%)	Elution Peak Height (mv)	Apparent Residual Life from Peak Heights(%) $\frac{(L - U)^2}{(L - C)^2} \times 100$
10% R.H.			
0	100	0.5	100
0.03	83	1.0	77
0.08	56	2.0	39
0.12	33	2.7	20
0.18	0	4.5	0
50% R.H.			
0	100	0.4	100
0.03	83	0.7	82
0.08	56	1.3	58
0.12	33	2.45	23
0.18	0	4.45	0
70% R.H.			
0	100	0.5	100
0.03	83	0.7	90
0.08	56	1.9	42
0.12	33	3.45	7
0.18	0	4.5	0

Table 8
Residual Life Calculated from MAA Adsorption and from CO_2 Elution Peak Heights at Three Relative Humidities

Weight of MAA per Gram of Charcoal (g/g)	Residual Life from MAA Adsorption (%)	Elution Peak Height (mv)	Apparent Residual Life from Peak Heights (%) $\frac{(L - U)^2}{(L - C)^2} \times 100$
10% R. H.			
0	100	0.75	100
0.08	56	1.7	62
0.12	33	2.4	40
0.14	22	3.8	10
0.16	11	4.5	3
0.18	0	5.2	0
50% R. H.			
0	100	0.6	100
0.08	56	1.5	65
0.12	33	2.4	38
0.14	22	3.95	8
0.16	11	4.55	3
0.18	0	5.3	0
70% R. H.			
0	100	0.80	100
0.08	56	1.8	64
0.12	33	2.75	37
0.14	22	4.1	11
0.16	11	4.7	5
0.18	0	5.75	0

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13. ABSTRACT

The CO_2 pulse method for determining the remaining adsorptive capacity, or residual gas life, of adsorbent charcoal beds has been carried out on a bench scale. This method depends on the dispersion, or broadening, of the CO_2 concentration pulse, or elution peak, when a dose of the gas is swept through the bed. A clean charcoal bed causes considerable dispersion of the elution peak; a fully spent bed has little effect. A partially spent bed broadens the elution peak to an extent which depends on the amount of adsorptive capacity remaining. This dispersion of the elution peak is essentially insensitive to relative humidity over the range from 10 to 70%. This method permits the nondestructive, in-place determination of residual gas life of a charcoal bed without interrupting its normal operation.

An adaptation of the CO_2 pulse method permits detection of leaks in a charcoal bed, such as those caused by channeling or faulty packing. A leak causes the CO_2 concentration pulse to emerge from the bed as a double peak-one lobe for the gas which penetrates the leak and the other for the gas which is eluted through the intact part of the bed.

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